



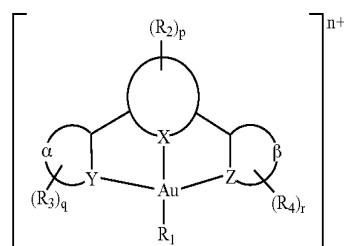
Title	Luminescent gold (III) compounds, their preparation, and light-emitting devices containing same
Inventor(s)	Yam, VWV; Wong, MC; Kwok Hoi-Sing; Zhu Xiuling
Citation	US Published patent application US 2006091378. Washington, DC: US Patent and Trademark Office (USPTO), 2006
Issued Date	2006
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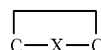
(19) **United States**(12) **Patent Application Publication****Yam et al.**(10) **Pub. No.: US 2006/0091378 A1**(43) **Pub. Date: May 4, 2006**(54) **LUMINESCENT GOLD (III) COMPOUNDS,
THEIR PREPARATION, AND
LIGHT-EMITTING DEVICES CONTAINING
SAME**(76) Inventors: **Vivian Wing-Wah Yam**, Hong Kong
(CN); **Man-Chung Wong**, Hong Kong
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AVENUE)****41 ST FL.****NEW YORK, NY 10036-2714 (US)**(21) Appl. No.: **10/977,200**(22) Filed: **Oct. 29, 2004****Publication Classification**(51) **Int. Cl.****H01L 29/08** (2006.01)**H01L 35/24** (2006.01)**C07F 1/12** (2006.01)(52) **U.S. Cl.** **257/40; 546/2**(57) **ABSTRACT**A class of luminescent gold(III) compounds with a tridentate ligand and at least one strong σ -donating group having the chemical structure represented by the general formula (I):

(I)

wherein R_1 - R_4 each independently represent the group containing hydrogen, halogen, alkynyl, substituted alkynyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, substituted alkoxy, amino, substituted amino, cyano, nitro, alkylcarbonyl, alkoxy carbonyl, arylcarbonyl, aryloxy carbonyl, mono- or dialkylaminocarbonyl, alkylcarbonyloxy, arylcarbonyloxy, aryloxy, alkoxy carbonyl, aryloxy carbonyloxy group, and the like; X, Y and Z each independently represent a heteroatom or a carbon;



represents an aromatic or heterocyclic 5- or 6-membered ring; α and β each independently represent a bridge for an aromatic or heterocyclic 5- or 6-membered ring or represent a break for non-cyclic moiety; C—X, C—Y and C—Z each independently represent a single bond or double bond; n represents a zero or an integer; p, q and r represent positive integers.

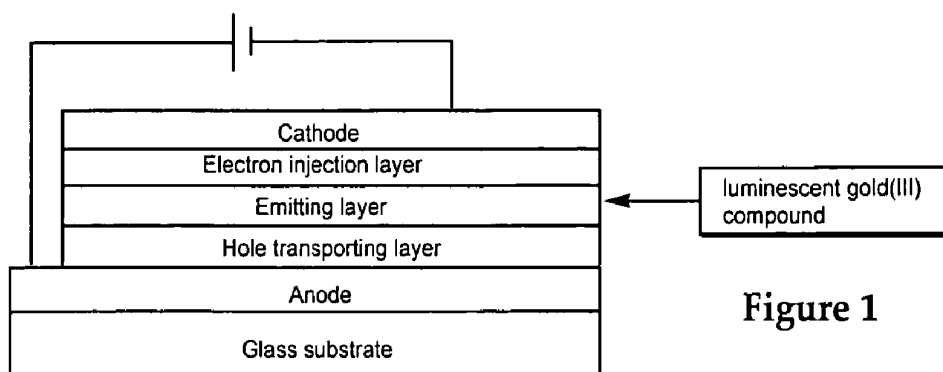


Figure 1

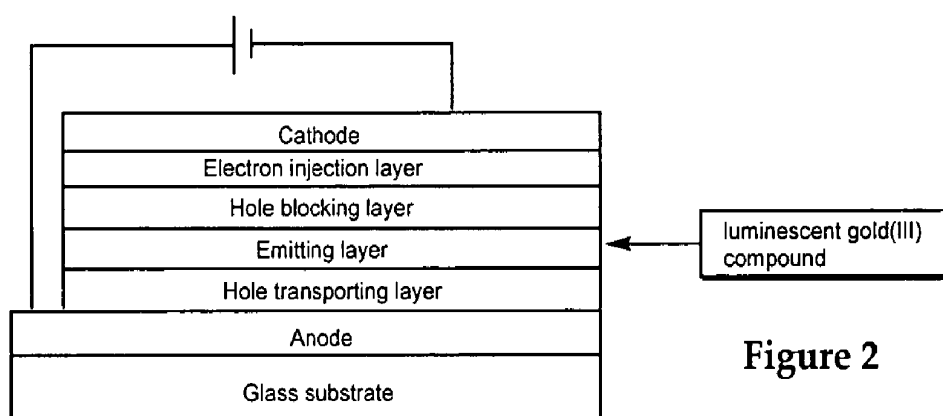


Figure 2

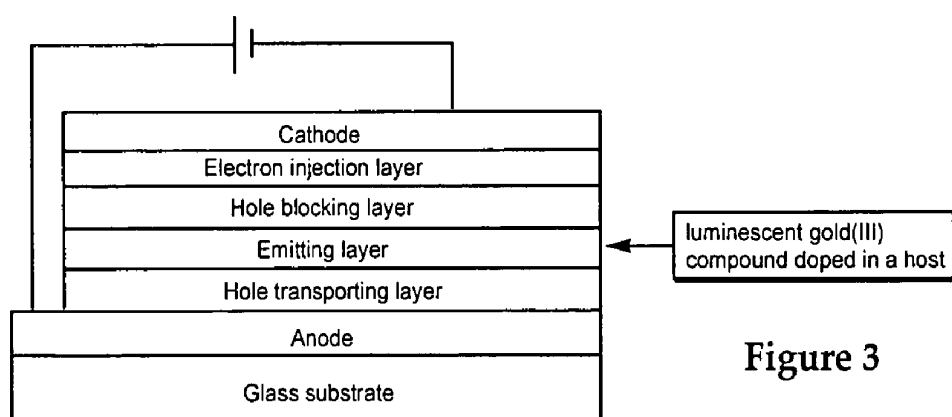


Figure 3

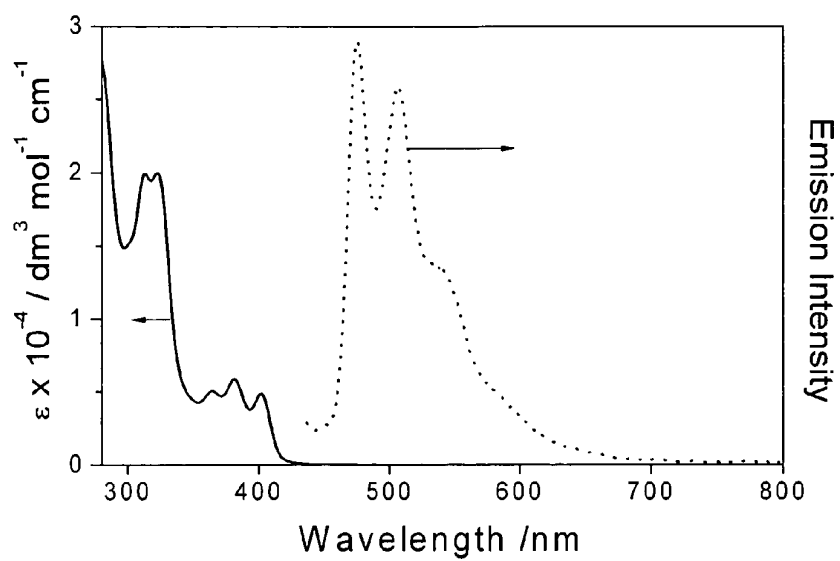


Figure 4

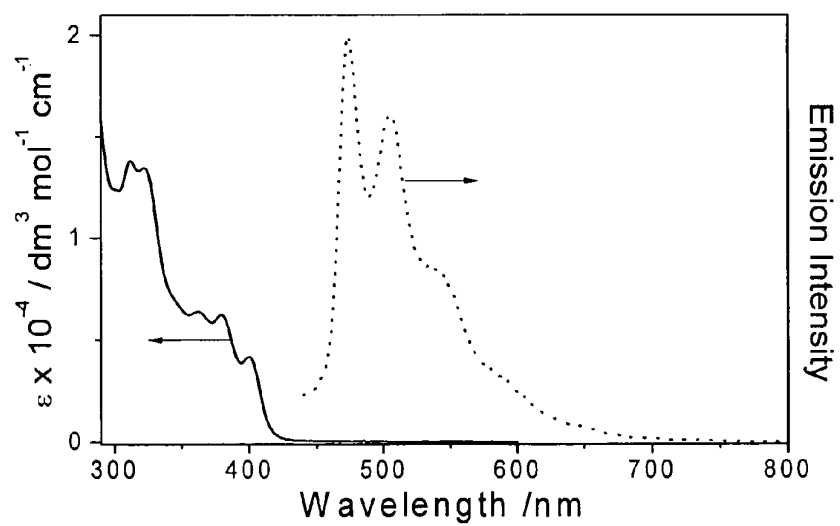


Figure 5

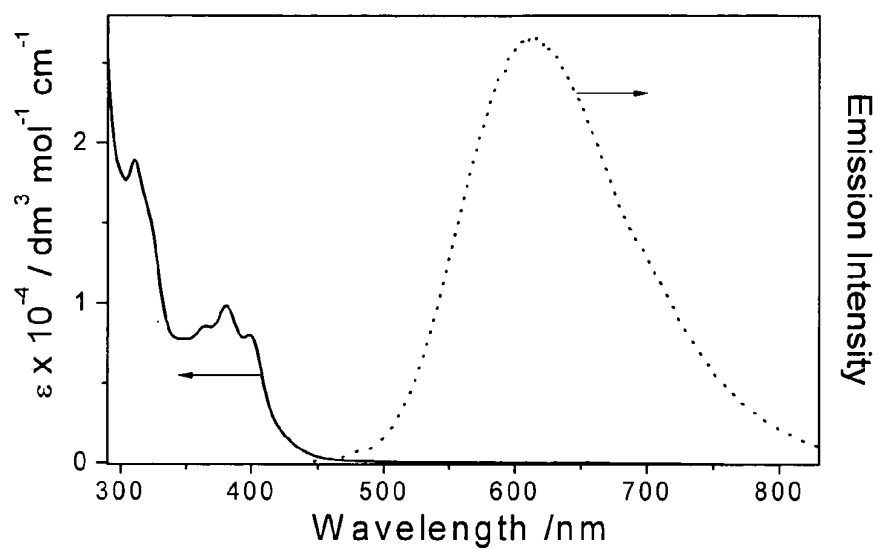


Figure 6

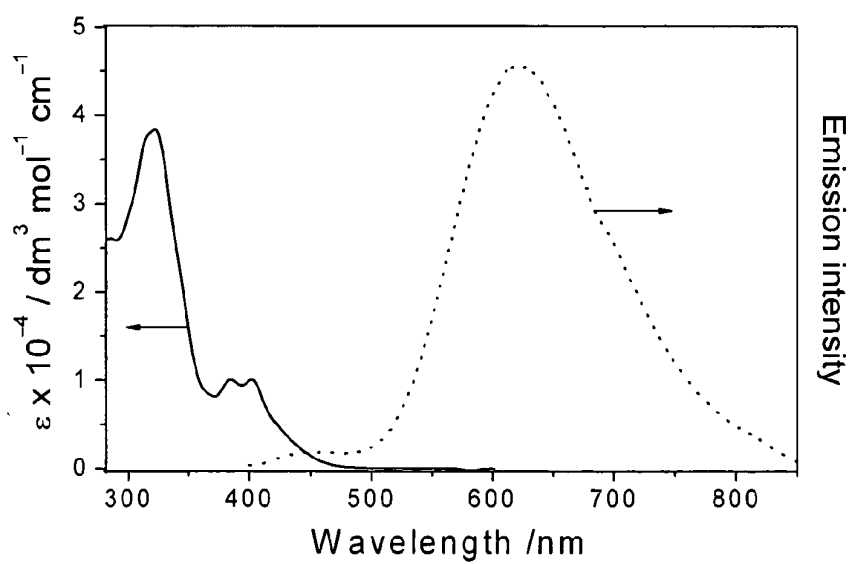


Figure 7

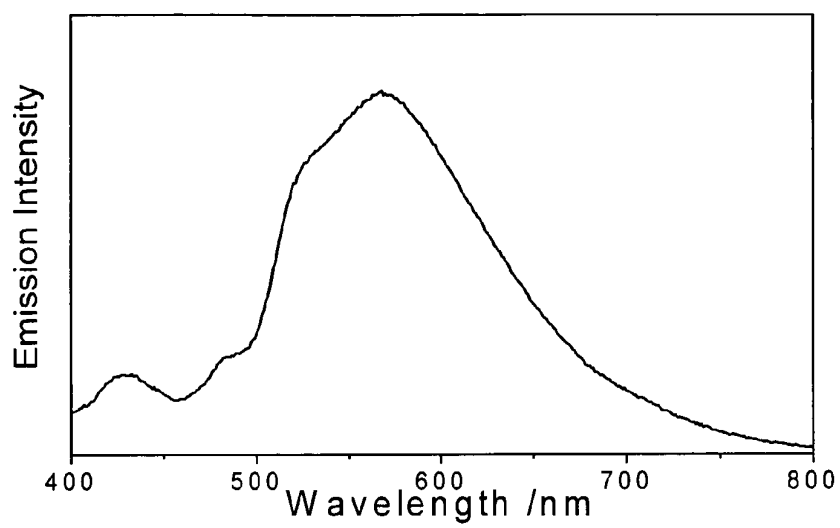


Figure 8

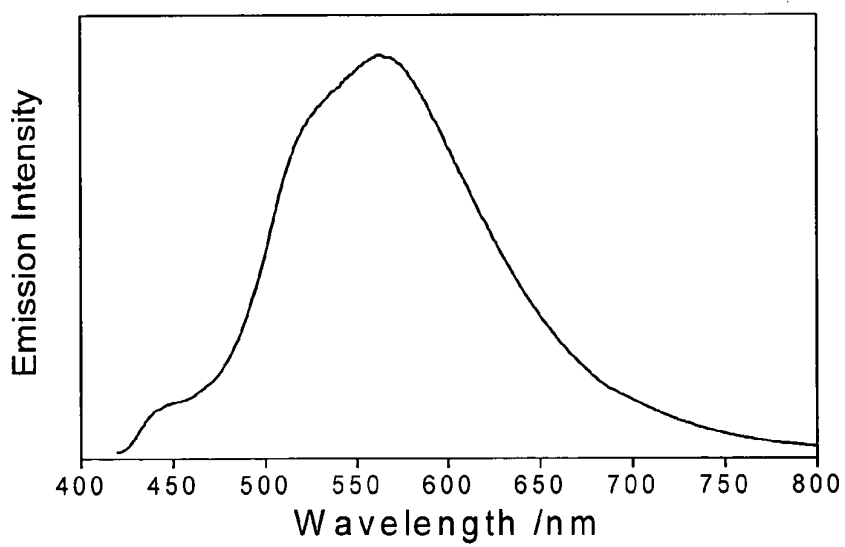


Figure 9

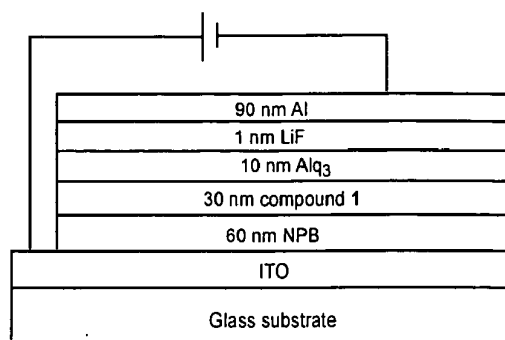


Figure 10A

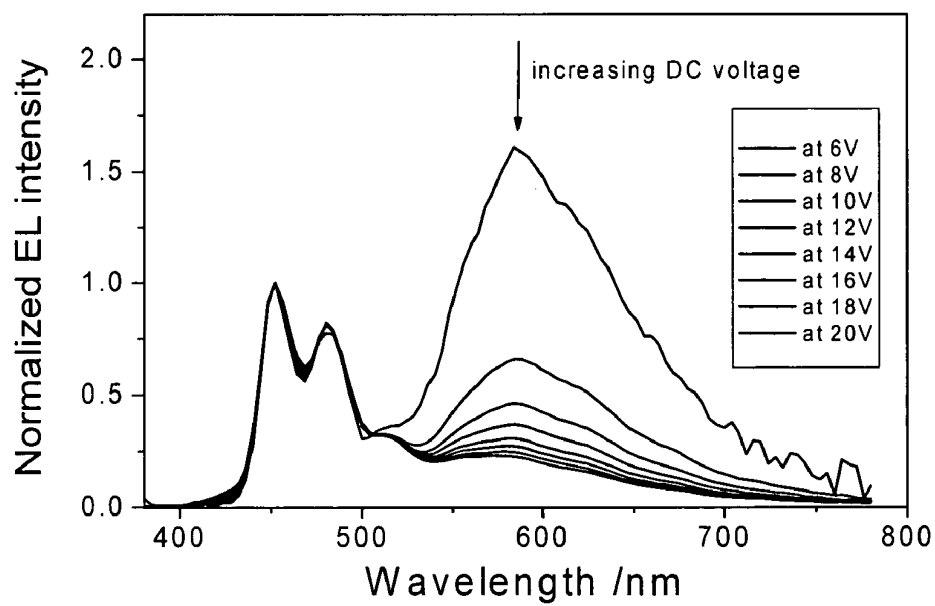


Figure 10B

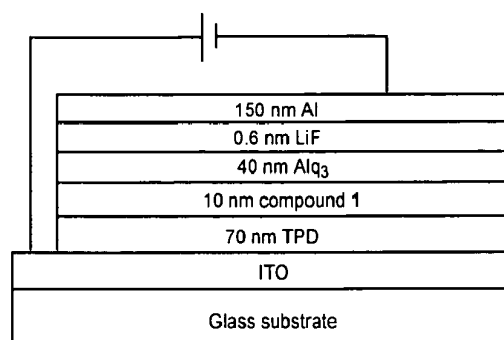


Figure 11A

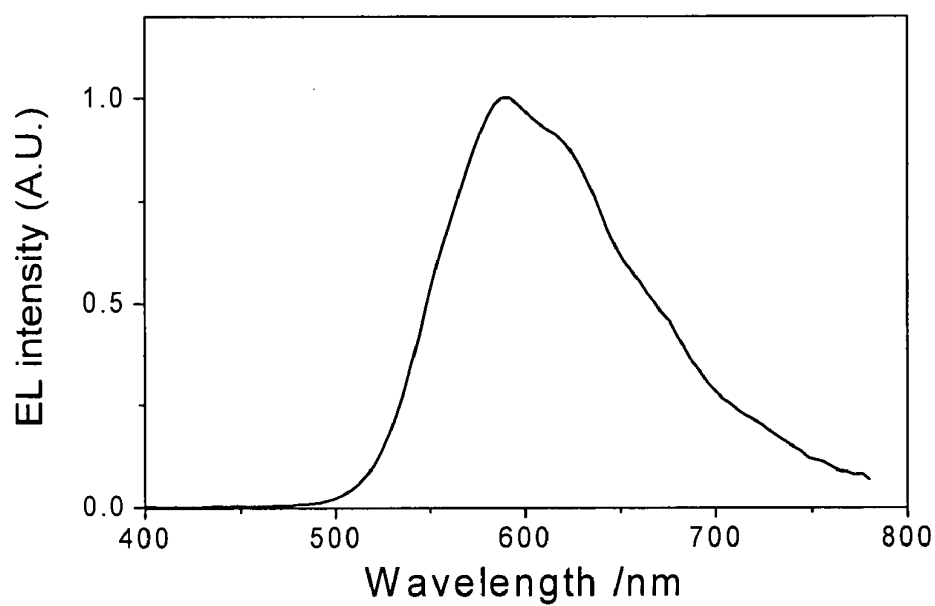


Figure 11B

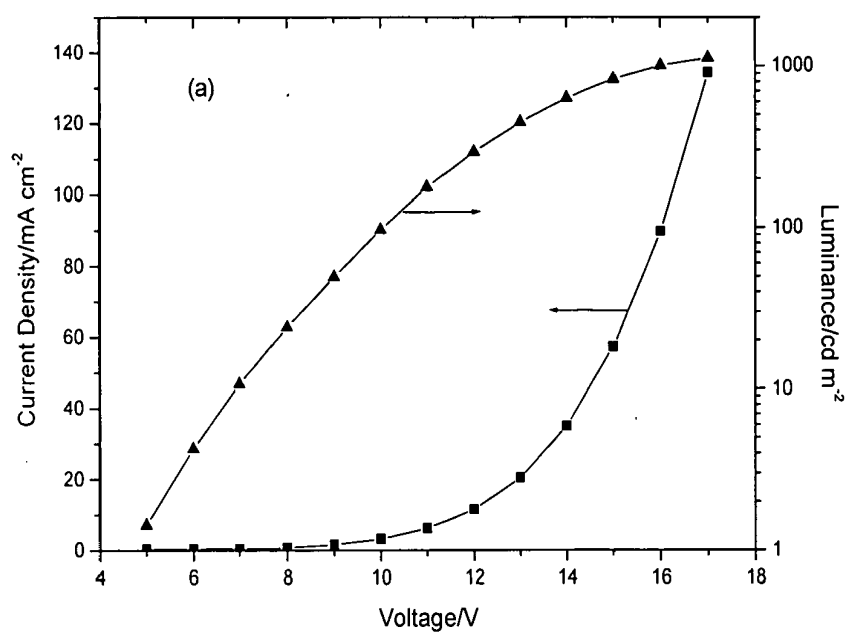


Figure 11C

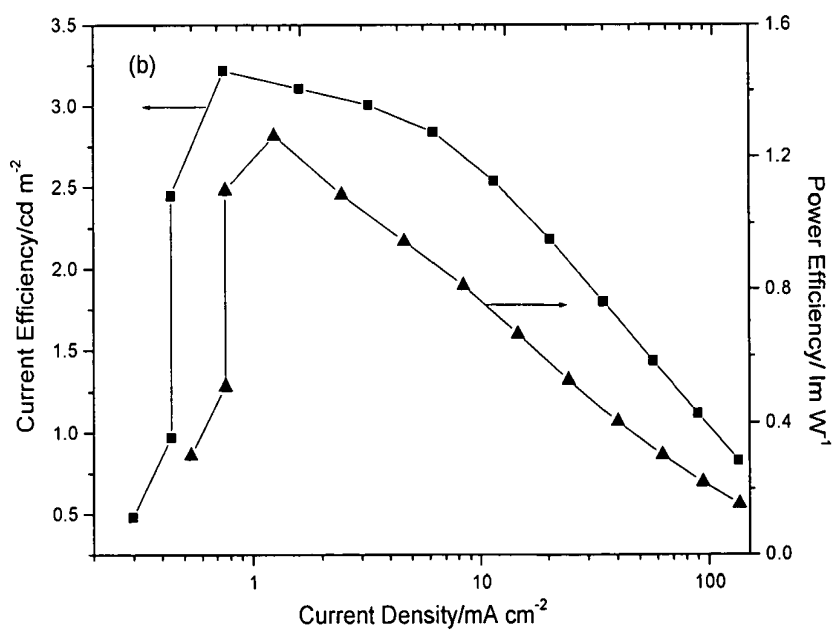


Figure 11D

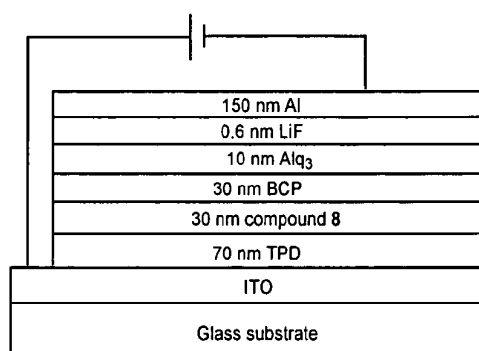


Figure 12A

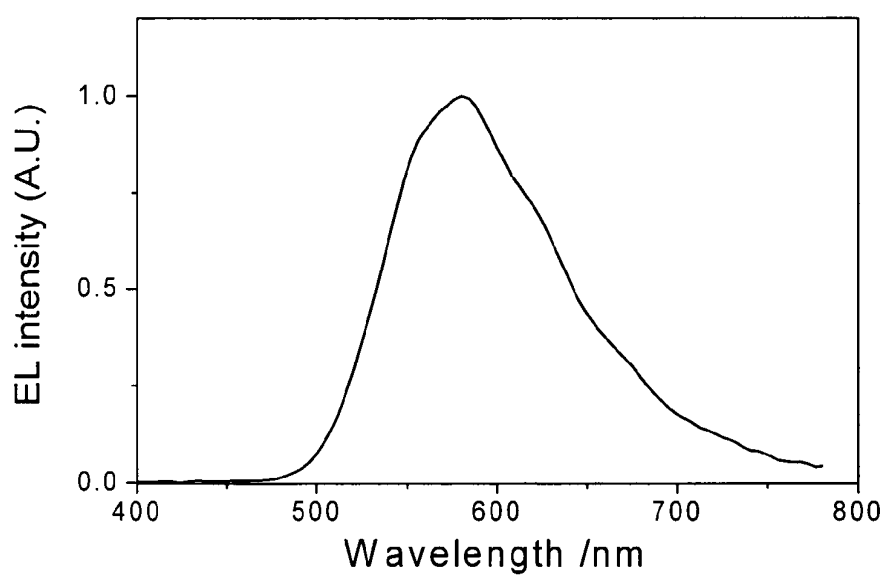


Figure 12B

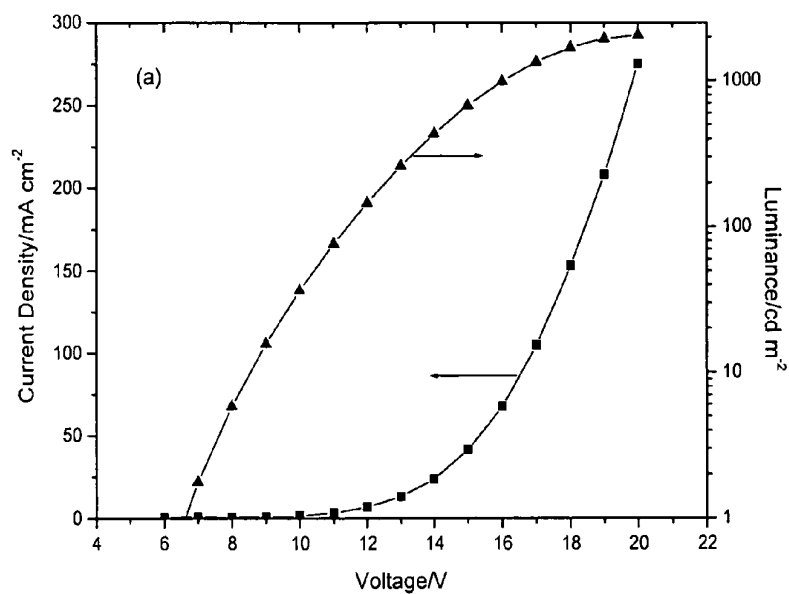


Figure 12C

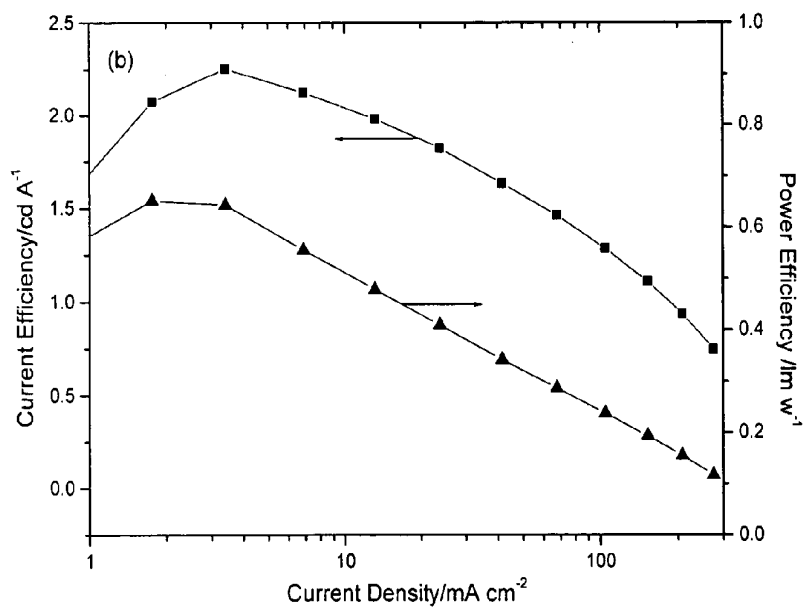


Figure 12D

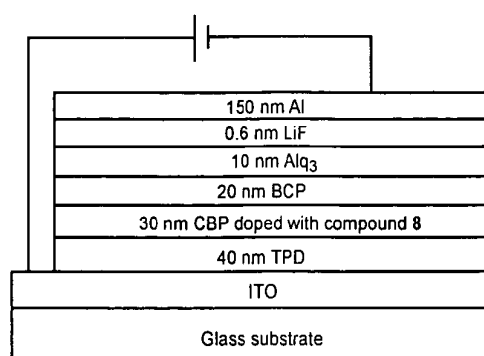


Figure 13A

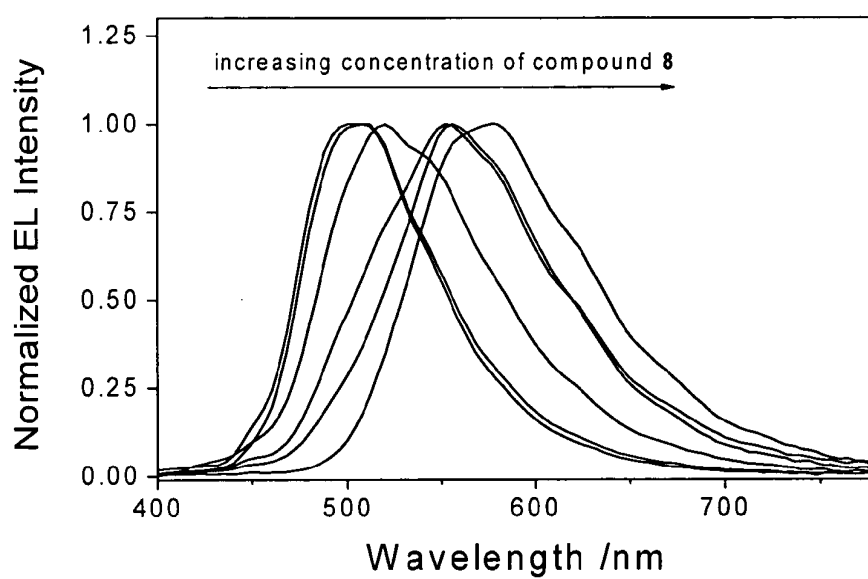


Figure 13B

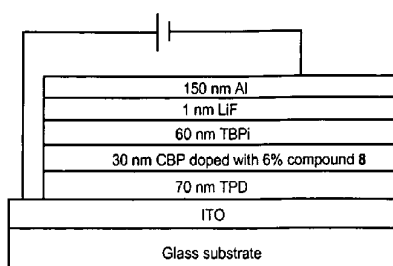


Figure 14A

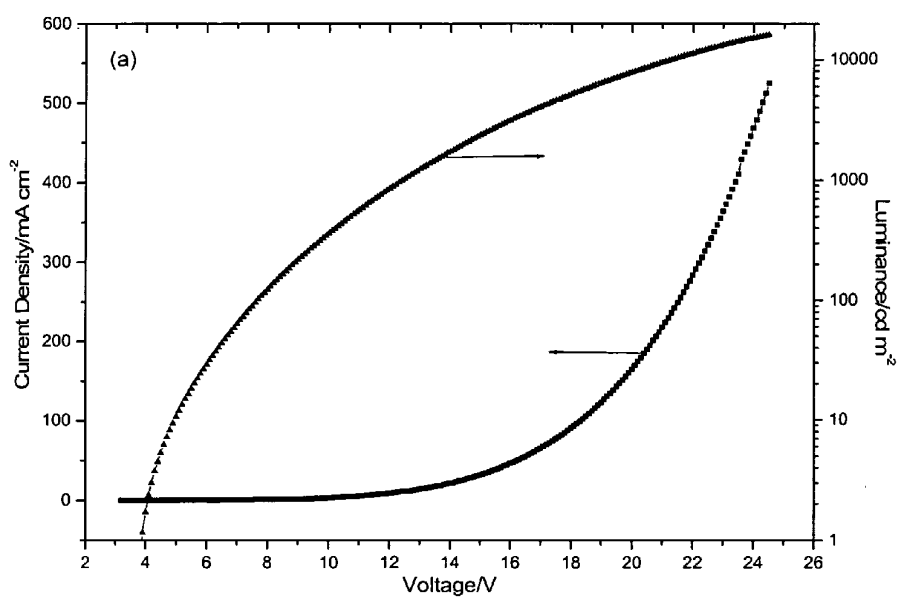


Figure 14B

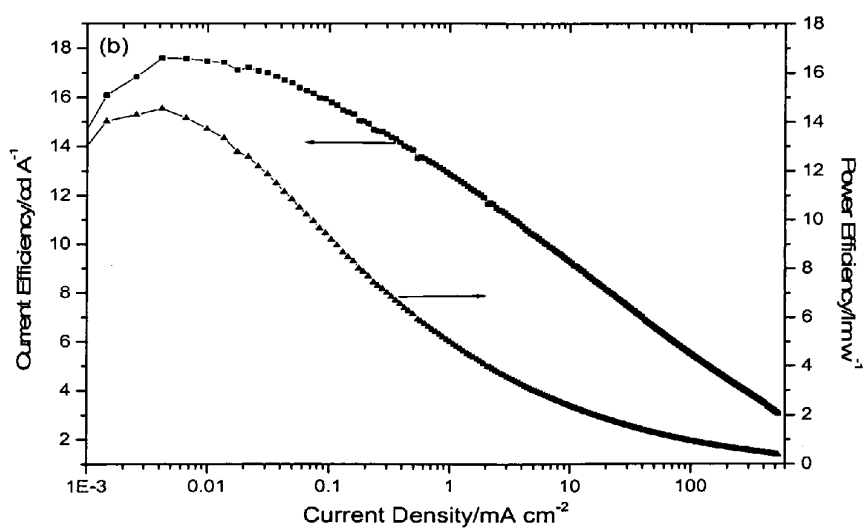


Figure 14C

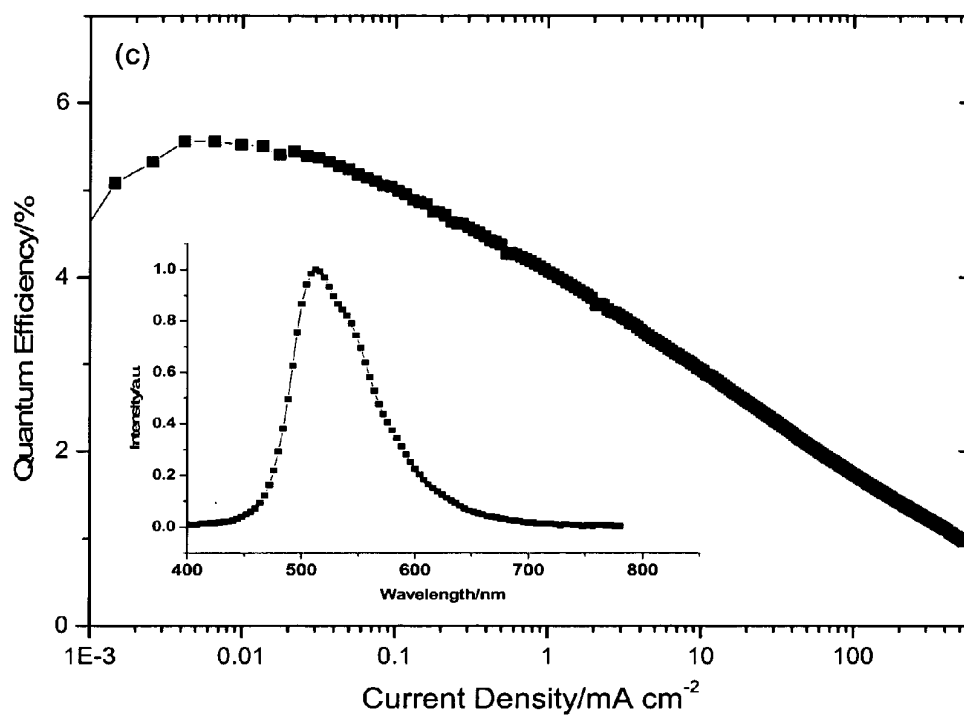


Figure 14D

LUMINESCENT GOLD (III) COMPOUNDS, THEIR PREPARATION, AND LIGHT-EMITTING DEVICES CONTAINING SAME

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] Not Applicable.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable.

INCORPORATION-BY-REFERENCE OF MATERIAL SUBMITTED ON A COMPACT DISK

[0003] Not Applicable.

BACKGROUND OF THE INVENTION

[0004] (1) Field of the Invention

[0005] The present invention is directed to a new class of luminescent gold(III) compounds containing a tridentate ligand and having at least one strong σ -donating group. Such compounds can be used as light-emitting material in phosphorescence based organic light-emitting devices (OLEDs), wherein different colors can be obtained by varying the applied DC voltage or the dopant concentration of said compounds.

[0006] (2) Description of Related Art Including Information Disclosed Under 37 C.F.R. 1.97 and 1.98.

[0007] The market for flat-panel displays has attracted considerable attention in connection with the development of electroluminescent materials. The electroluminescence materials used are generally categorized into conjugated polymers or low-molar-mass small molecules. OLEDs are among the most important candidates for the use of electroluminescent materials in commercial flat-panel displays because OLEDs possess the advantages of robustness, ease of fabrication and color tuning, wide viewing angle, high brightness and contrast ratios, low turn-on voltage and low energy consumption.

[0008] A typical OLED structure is composed of a thin film of organic material sandwiched between a transparent conductor such as indium tin oxide (ITO), and a vapor deposited metal cathode. Upon applying an electrical potential, excitons are formed by the recombination of the holes and electrons, injected from the ITO electrode and metal cathode, respectively. Electroluminescence is generated in the organic material from the radiative relaxation of excitons. Higher performance of the device can be achieved by using multiple organic layers for separation of hole and electron transporting layers.

[0009] Although electroluminescence from organic polymers was initially reported years ago [Kaneto, K.; Yoshino, K.; Koa, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* 18, 1023 (1974)], it was only after the report on yellow-green electroluminescence from poly(p-phenylenevinylene) (PPV) that light-emitting polymers and OLEDs have received much attention [Burroughs, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, N.; Friend, R. H.; Burn, P. L.; Holmes, A. B., *Nature* 347, 539 (1990)]. Later on, similar studies were reported by using

PPV derivatives as the light-emitting polymers [Braun, D.; Heeger, A. J., *Appl. Phys. Lett.* 58, 1982 (1991)]. Since then a number of new electroluminescent polymers have been investigated for improved properties.

[0010] Electroluminescence of organic materials was discovered in anthracene crystals immersed in liquid electrolyte in 1965 [Helfrich, W.; Schneider, W. G. *Phys. Rev. Lett.* 14, 229 (1965)]. Although lower operating voltages could be achieved by using a thin film of anthracene as well as solid electrodes, very low efficiency of such a single-layer device was encountered. High-performance green electroluminescence from an organic small molecule, aluminum tris(quinolate) (Alq_3), was first reported in 1987 [Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* 51, 913 (1987)]. A double-layer OLED with high efficiency and low operating voltage was described, in which Alq_3 was utilized both as emitting layer and electron transporting layer. Subsequent modifications of the device with triple-layer structure gave better performance with higher efficiency.

[0011] Some improvements in OLED efficiencies have been achieved by using phosphorescent material to generate light emission from both singlet and triplet excitons. One approach, particularly for small-molecule OLEDs, is to harvest triplet excitons efficiently through incorporation of heavy metal centers, which would increase spin-orbit coupling and hence intersystem crossing into the triplet state. In 1998, Baldo et al. demonstrated a phosphorescence electroluminescence device with high quantum efficiency by using platinum(II) 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine (PtOEP) as a dye [Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* 395, 151 (1998)]. A multilayer device in which the emitting layer of Alq_3 is doped with PtOEP showed a strong emission at 650 nm attributed to the triplet excitons of PtOEP. Cyclometalated iridium(III) is known to show phosphorescence and is another class of materials used for high efficiency OLEDs. Baldo et al. reported the use of fac-tri(2-phenylpyridine)iridium(III) [Ir(ppy)_3] as phosphorescence emitting material which was doped in 4,4'-N,N'-dicarbazole-biphenyl (CBP) as a host in an OLED to give high quantum efficiency [Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* 75, 4 (1999)]. In addition, fac-tri(2-phenylpyridine)iridium(III) [Ir(ppy)_3] was used as phosphorescence sensitizer for high efficiency fluorescent OLED [Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature*, 403, 750 (2000)]. Using the concept of a phosphorescence emitter with a higher population of excitations, very high efficiency red fluorescence from [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[II]quinolizin-9-yl)-ethenyl]-4H-pyran-4-ylidene]propanedinitrile (DCM2) was found in a multilayer OLED composed of Ir(ppy)_3 and DCM2 dopant layers. In a sensitization process, energy is transferred from Ir(ppy)_3 to DCM2 to give such high efficiency fluorescence.

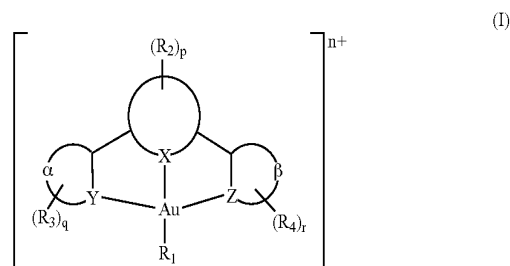
[0012] Apart from the enhancement of the emission efficiency, the ability to bring about a variation in the emission color would be important. Most of the common approaches involve the use of different light-emitting materials or multi-component blended mixtures of light-emitting materials with different emission characteristics for color tuning. Examples that employ a single light-emitting material as dopant to generate more than one emission color have been rare. Recent studies have shown that different emission

colors from a single emissive dopant could be generated by using phosphorescent material through a change in the direction of the bias or in the dopant concentration. Welter et al. reported the fabrication of a simple OLED consisting of semiconducting polymer PPV and phosphorescent ruthenium polypyridine dopant [Welter, S.; Krunner, K.; Hofstraat, J. W.; De Cola, D. *Nature*, 421, 54 (2003)]. At forward bias, red emission from the excited state of the phosphorescent ruthenium polypyridine dopant was observed, while the OLED emitted a green emission at reverse bias in that the lowest excited singlet state of PPV was populated. Adamovich et al. reported the use of a series of phosphorescent platinum(II) [2-(4,6-difluorophenyl)pyridinato-N,C²] β -diketonates as single emissive dopant in OLED [Adamovich, V.; Brooks, J.; Tamayo, A.; Alexander, A. M.; Djurovich, P. R.; D'Andrade, B. W.; Adachi, C.; Forrest, S. R.; Thompson, M. E. *New J. Chem.* 26, 1171 (2002)]. Both blue emission from the monomeric species and orange emission from the aggregates were observed in such OLED and the relative intensity of the orange emission increases as the doping level is increased. As a result, the electroluminescence color can be tuned by changing the dopant concentration, and white illumination sources of an OLED can be obtained in a doping concentration with equal intensities of the monomeric and aggregate bands. In both cases, the change of electroluminescence color in OLED can be accomplished upon a variation of the external stimulus or fabrication conditions while keeping the light-emitting material the same.

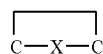
[0013] Despite recent interest in electrophosphorescent materials, in particular metal complexes with heavy metal centers, most of the work has been focused on the use of iridium(III), platinum(II) and ruthenium(II), while other metal centers have been relatively less extensively explored. In contrast to the isoelectronic platinum(II) compounds which are known to show rich luminescence properties, very few examples of luminescent gold(III) compounds have been reported, probably due to the presence of low-energy d-d ligand field (LF) states and the electrophilicity of the gold(III) metal center. The introduction of strong σ -donating ligands into gold(III) compounds to enhance the luminescence properties as a result of the enlargement of d-d splitting has been considered. Yam et al. first demonstrated that gold(III) aryl compounds are photo-stable and are capable of displaying interesting photoluminescence properties which occur even at room temperature [Yam, V. W. W.; Choi, S. W. K.; Lai, T. F.; Lee, W. K. *J. Chem. Soc., Dalton Trans.* 1001(1993)]. Another interesting donor ligand is the alkynyl group. But despite the fact that a number of gold(I) alkynyls are known and have been shown to exhibit interesting luminescence properties, the chemistry of gold(III) alkynyls has been essentially ignored, except for a brief report on the synthesis of an alkynylgold(III) compound of 6-benzyl-2,2'-bipyridine in the literature [Cinellu, M. A.; Minghetti, G.; Pinna, M. V.; Stoccoro, S.; Zucca, A.; Manassero, M. *J. Chem. Soc. Dalton Trans.* 2823 (1999)], but their luminescence behaviour has remained totally unexplored. The present inventors have described herein the design, synthesis and photoluminescence behaviors of luminescent gold(III) compounds with a tridentate ligand and at least one strong σ -donating group, and the use of such compounds as electrophosphorescent material in OLEDs to give strong electroluminescence with high efficiency.

BRIEF SUMMARY OF THE INVENTION

[0014] The present invention is directed to novel luminescent gold(III) compounds, their preparation, and OLEDs containing them. The compounds have the chemical structure shown in generic formula (I):



wherein R₁, R₂, R₃ and R₄ each independently represents a substituent selected from the group consisting of hydrogen, halogen, alkynyl, substituted alkynyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, substituted alkoxy, amino, substituted amino, cyano, nitro, alkylcarbonyl, alkoxy carbonyl, arylcarbonyl, aryloxy carbonyl, mono- or dialkylaminocarbonyl, alkylcarbonyloxy, arylcarbonyloxy, aryloxy, alkoxy carbonyl, aryloxy carbonyloxy group, and the like; X, Y and Z each independently represent a heteroatom or a carbon;



represents an aromatic or heterocyclic 5- or 6-membered ring; α and β each independently represents a bridge for an aromatic or heterocyclic 5- or 6-membered ring, or a break for a non-cyclic moiety; C—X, C—Y and C—Z each independently represents a single bond or double bond; n is a zero or an integer; and p, q and r are positive integers. The compounds of the present invention each contains one tridentate ligand and at least one strong σ -donating group coordinating to a gold(III) metal center.

[0015] The luminescent gold(III) compounds of the present invention show photoluminescence via triplet excited state upon photo-excitation, or electroluminescence via triplet exciton upon applying a DC voltage. Preferred compounds of the invention are thermally stable and volatile enough to be able to form a thin layer by sublimation or vacuum deposition.

[0016] The present invention is also directed to the use of luminescent compounds of general formula (I) as phosphorescent emitters or dopants fabricated into OLEDs to generate electroluminescence. In one embodiment, the light-emitting material used as a phosphorescent emitter or dopant in an OLED can comprise a gold(III) compound coordinated with one tridentate ligand and at least one strong σ -donating ligand.

[0017] In an OLED according to the present invention, the luminescent compound is included in a light-emitting layer or as a dopant arranged between a pair of electrodes. The typical structure of an OLED using the luminescent com-

pound of the present invention as a light-emitting layer without an electron blocking layer is in the order shown in **FIG. 1**: anode/hole transporting layer/luminescent gold(III) compound as a light-emitting layer/electron injection layer/cathode.

[0018] The typical structure of an OLED using the luminescent compound of the present invention as a light-emitting layer with an electron blocking layer is in the order shown in **FIG. 2**: anode/hole transporting layer/luminescent gold(III) compound as light-emitting layer/hole blocking layer/electron injection layer/cathode.

[0019] The typical structure of an OLED using the luminescent compound of the present invention as a dopant with an electron blocking layer is in the order shown in **FIG. 3**: anode/hole transporting layer/luminescent gold(III) compound doped in host/hole blocking layer/electron transporting layer/cathode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] **FIG. 1** shows the structure of an OLED using the luminescent compound of the present invention as the light-emitting layer without an electron blocking layer.

[0021] **FIG. 2** shows the structure of an OLED using the luminescent compound of the present invention as the light-emitting layer with an electron blocking layer.

[0022] **FIG. 3** shows the structure of an OLED using the luminescent copolymer of the present invention as a dopant with an electron blocking layer.

[0023] **FIG. 4** shows the UV-vis absorption and emission spectra of compound 1 in dichloromethane at 298° K. No instrumental correction was applied for the emission wavelength.

[0024] **FIG. 5** shows the UV-vis absorption and emission spectra of compound 4 in dichloromethane at 298° K. No instrumental correction was applied for the emission wavelength.

[0025] **FIG. 6** shows the UV-vis absorption and emission spectra of compound 6 in dichloromethane at 298° K. No instrumental correction was applied for the emission wavelength.

[0026] **FIG. 7** UV-vis absorption and emission spectra of compound 8 in dichloromethane at 298° K. No instrumental correction was applied for the emission wavelength.

[0027] **FIG. 8** shows the solid state (thin film) emission spectrum of compound 1 at 298° K. No instrumental correction was applied for the emission wavelength.

[0028] **FIG. 9** shows the solid state (thin film) emission spectrum of compound 8 at 298° K. No instrumental correction was applied for the emission wavelength.

[0029] **FIG. 10A** shows the multilayer OLED with the structure of ITO/NPB (60 nm)/compound 1 (30 nm)/Alq₃ (10 nm)/LiF (1 nm)/Al (90 nm).

[0030] **FIG. 10B** shows the electroluminescence spectra of device 1 (see **FIG. 1**) at different applied DC voltages; the emission intensities are normalized in the range of 450-480 nm.

[0031] **FIG. 11A** shows the multilayer OLED of device 2 (see **FIG. 2**) with the structure of ITO/TPD (70 nm)/compound 1 (10 nm)/Alq₃ (40 nm)/LiF (0.6 nm)/Al (150 nm).

[0032] **FIG. 11B** shows the electroluminescence spectrum of device 2 (see **FIG. 2**) upon applying 7 V DC voltage.

[0033] **FIG. 11C** shows the current density and luminance versus voltage characteristics of device 2 (see **FIG. 2**).

[0034] **FIG. 11D** shows the current and power efficiency versus current density characteristics of device 2 (see **FIG. 2**).

[0035] **FIG. 12A** shows the multilayer OLED with the structure of device 3 (see **FIG. 3**) ITO/TPD (70 nm)/compound 8 (30 nm)/BCP (30 nm)/Alq₃ (10 nm)/LiF (0.6 nm)/Al (150 nm).

[0036] **FIG. 12B** shows the electroluminescence spectrum of device 3 (see **FIG. 3**) upon applying 9 V DC voltage.

[0037] **FIG. 12C** shows the current density and luminance versus voltage characteristics of device 3 (see **FIG. 3**).

[0038] **FIG. 12D** shows the current and power efficiency versus current density characteristics of device 3 (see **FIG. 3**).

[0039] **FIG. 13A** shows the multilayer OLED of device 4 with the structure: ITO/TPD (40 nm)/CBP doped with (X %) compound 8 (30 nm)/BCP (20 nm)/Alq₃ (10 nm)/LiF (0.6 nm)/Al (150 nm) [X=1 (device 4a), 3 (device 4b), 6 (device 4c), 12 (device 4d), 18 (device 4e), 100 (device 4f)].

[0040] **FIG. 13B** shows normalized electroluminescence spectra of devices 4a-f with different concentrations of compound 81% (device 4a), 3 (device 4b), 6 (device 4c), 12 (device 4d), 18 (device 4e), 100 (device 4f) as dopant upon applying 12 V DC voltage.

[0041] **FIG. 14A** shows device 5: ITO/TPD (70 nm)/CBP (compound 8, 6 wt %) (30 nm)/TPBi (60 nm)/LiF (1 nm)/Al (150 nm).

[0042] **FIG. 14B** shows a plot of current density and luminance versus voltage for device 5.

[0043] **FIG. 14C** shows a plot of current and power efficiency versus current density for device 5.

[0044] **FIG. 14D** plot of quantum efficiency versus current density. Inset: spectra characteristics of device 5.

DETAILED DESCRIPTION OF THE INVENTION

[0045] The present invention is related to the syntheses, spectral characterization, and luminescence properties of a class of luminescent gold(III) compounds with one tridentate ligand and at least one strong σ -donating group; and the use of such compounds as light-emitting material in OLEDs to provide electroluminescence with high efficiency and brightness. The compounds have the following structural characteristics:

[0046] (1) at least one gold metal center at an oxidation state of +3;

[0047] (2) said one gold metal center having four coordination sites;

[0048] (3) one tridentate ligand with one to three aromatic or heterocyclic ring(s) coordinating to the gold metal center;

[0049] (4) one monodentate ligand coordinating to the gold metal center;

[0050] (5) at least one strong σ -donating ligand coordinating to the gold metal center; and

[0051] (6) the compounds being charged or neutral.

[0052] Gold(III) compounds have been rarely observed to emit, in contrast to their isoelectronic platinum(II) compounds which are known to display rich luminescence properties. The lack of luminescence behavior in gold(III) compounds may be due to the presence of low-lying d-d ligand field (LF) states and the electrophilicity of the gold(III) metal center. Gold(III) aryl compounds [Yam, V. W. W.; Choi, S. W. K.; Lai, T. F.; Lee, W. K. *J. Chem. Soc., Dalton Trans.* 1001(1993)] are exceptions in that they show interesting luminescence properties even at room temperature and possess photo-stability upon light irradiation. Without wishing to be bound by theory, it is believed that the coupling of strong σ -donating ligands to gold(III) renders the metal centre more electron-rich, thereby raising the energy of the d-d states, which results in an improvement or enhancement of the luminescence by increasing the chances for population of the emissive state. A class of luminescent gold(III) compounds with one tridentate ligand and at least one strong σ -donating group will be described in detail hereinbelow.

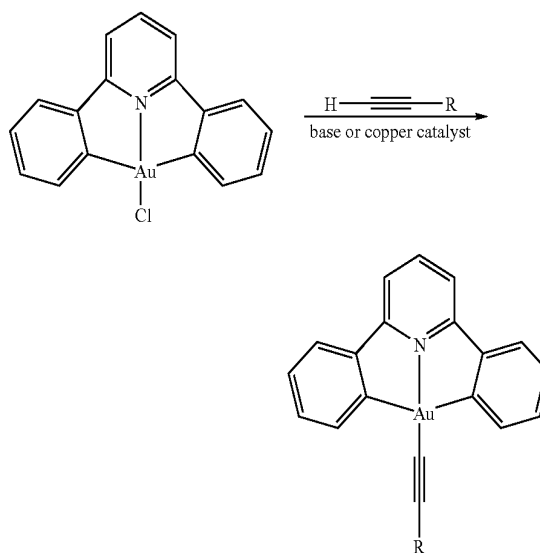
[0053] The luminescent gold(III) compounds of the present invention can be formed into thin films by vacuum deposition, spin-coating or other known fabrication methods. Different multilayer OLEDs have been fabricated using the compounds of the present invention as light-emitting material or as dopant in the emitting layer. In general, the OLEDs consist of one anode and one cathode, between which are the hole transporting layer, light-emitting layer, and electron transporting or injection layer.

[0054] The present invention will be illustrated more specifically by the following non-limiting examples, it being understood that changes and variations can be made therein without deviating from the scope and the spirit of the invention as hereinafter claimed.

EXAMPLE 1

Synthesis and Characterization

[0055] Compounds 1-8 were synthesized according to the following methodology. The precursor compound, $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}]$, was prepared according to the modification of a procedure reported in the literature [Wong, K. H.; Cheung, K. K.; Chan, M. C. W.; Che, C. M. *Organometallics*, 17, 5305(1998)]. The desired compounds were synthesized by the reaction of $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}]$ with various alkynes in the presence of a base or copper catalyst in an organic solvent. For example, to a mixture of $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}]$, terminal alkyne and Et_3N in degassed dichloromethane solution was added CuI . The reaction mixture was stirred for 6 hours under a nitrogen atmosphere at room temperature. The crude product was purified by column chromatography on silica gel using dichloromethane as eluent. Pale yellow crystals were obtained from slow diffusion of diethyl ether into the dichloromethane solution of the compounds.



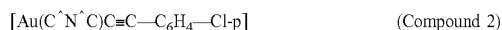
R =

C_6H_5	(1)
$\text{C}_6\text{H}_4\text{—Cl-p}$	(2)
$\text{C}_6\text{H}_4\text{—NO}_2\text{-p}$	(3)
$\text{C}_6\text{H}_4\text{—OCH}_3\text{-p}$	(4)
$\text{C}_6\text{H}_4\text{—C}_6\text{H}_{13}\text{-p}$	(5)
$\text{C}_6\text{H}_4\text{—NH}_2\text{-p}$	(6)
C_6H_{13}	(7)
$\text{C}_6\text{H}_4\text{—N}(\text{C}_6\text{H}_5)_2\text{-p}$	(8)

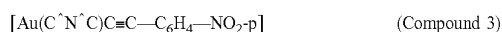
[0056] The characteristic spectral properties of compounds 1-8 are as follows:



[0057] Yield: 88%. ^1H NMR (300 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.04 (dd, 7.4 and 1.0 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.92 (t, 8.0 Hz, 1H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.62 (m, 4H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ and C_6H_5), 7.54 (d, 8.0 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.26-7.44 (m, 7H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ and C_6H_5); positive EI-MS: m/z 527 $[\text{M}]^+$; IR (KBr): 2147 cm^{-1} $\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{25}\text{H}_{16}\text{NAu}$ (found): C 56.93 (56.57), H 3.04 (3.05), N 2.66 (2.66).



[0058] Yield: 85%. ^1H NMR (300 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.00 (dd, 7.2 and 1.0 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.90 (t, 8.0 Hz, 1H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.50-7.60 (m, 6H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ and C_6H_4), 7.25-7.42 (m, 6H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ and C_6H_4); positive EI-MS: m/z 562 $[\text{M}]^+$; IR (KBr): 2157 cm^{-1} $\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{25}\text{H}_{15}\text{NClAu} \cdot \frac{1}{2}\text{H}_2\text{O}$ (found): C 52.59 (52.85), H 2.80 (2.66), N 2.45 (2.40).



[0059] Yield: 80%. ^1H NMR (400 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.22 (d, 9.0 Hz, 2H, C_6H_4), 8.00 (dd, 7.6 and 1.2 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.94 (t, 8.0 Hz, 1H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.73 (d, 9.0 Hz, 2H, C_6H_4), 7.64 (dd, 7.6 and 1.2 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.55 (d, 8.0 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.41 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.32 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$); positive EI-MS: m/z 572 $[\text{M}]^+$; IR (KBr): 2146 cm^{-1}

$\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{25}\text{H}_{15}\text{N}_2\text{O}_2\text{Au}$ (found): C 51.64 (51.62), H 2.75 (2.69), N 4.82 (4.75).

$[\text{Au}(\text{C}\equiv\text{N}\text{C})\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{OCH}_3\text{-p}]$ (Compound 4)

[0060] Yield: 86%. ^1H NMR (400 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.02 (dd, 7.6 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.90 (t, 8.0 Hz, 1H, $\text{C}\equiv\text{N}\text{C}$), 7.60 (dd, 7.6 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.50-7.56 (m, 4H, $\text{C}\equiv\text{N}\text{C}$ and C_6H_4), 7.40 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.27 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 6.91 (d, 8.9 Hz, 2H, C_6H_4), 3.88 (s, 3H, OCH_3); positive EI-MS: m/z 557 $[\text{M}]^+$; IR (KBr): 2157 cm^{-1} $\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{26}\text{H}_{18}\text{NOAu}\cdot\frac{1}{2}\text{H}_2\text{O}$ (found): C 55.12 (55.15), H 3.36 (3.28), N 2.47 (2.48).

$[\text{Au}(\text{C}\equiv\text{N}\text{C})\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_{13}\text{-p}]$ (Compound 5)

[0061] Yield: 75%. ^1H NMR (300 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.00 (dd, 7.4 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.87 (t, 8.0 Hz, 1H, $\text{C}\equiv\text{N}\text{C}$), 7.57 (dd, 7.4 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.47-7.51 (m, 4H, $\text{C}\equiv\text{N}\text{C}$ and C_6H_4), 7.37 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.24 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.18 (d, 8.3 Hz, 2H, C_6H_4), 2.64 (t, 7.7 Hz, 2H, $\text{CH}_2-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$), 1.64 (m, 2H, $\text{CH}_2-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$), 1.34 (m, 6H, $\text{CH}_2-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$), 0.90 (t, 7.0 Hz, 3H, $\text{CH}_2-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$); positive EI-MS: m/z 611 $[\text{M}]^+$; IR (KBr): 2149 cm^{-1} $\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{31}\text{H}_{28}\text{NAu}\cdot\frac{1}{2}\text{H}_2\text{O}$ (found): C 60.00 (59.91), H 4.68 (4.60), N 2.26 (2.25).

$[\text{Au}(\text{C}\equiv\text{N}\text{C})\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{NH}_2\text{-p}]$ (Compound 6)

[0062] Yield: 80%. ^1H NMR (300 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.07 (dd, 7.4 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.92 (t, 8.0 Hz, 1H, $\text{C}\equiv\text{N}\text{C}$), 7.65 (dd, 7.4 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.56 (d, 8.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.39-7.45 (m, 4H, $\text{C}\equiv\text{N}\text{C}$ and C_6H_4), 7.30 (dt, 7.5 and 1.3 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 6.67 (d, 8.6 Hz, 2H, C_6H_4), 3.84 (s, 2H, NH_2); positive EI-MS: m/z 542 $[\text{M}]^+$; IR (KBr): 2143 cm^{-1} $\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{25}\text{H}_{17}\text{N}_2\text{Au}\cdot\frac{1}{2}\text{H}_2\text{O}$ (found): C 54.45 (54.59), H 3.27 (3.13), N 5.08 (5.04).

$[\text{Au}(\text{C}\equiv\text{N}\text{C})\text{C}\equiv\text{C}-\text{C}_6\text{H}_{13}]$ (Compound 7)

[0063] Yield: 85%. ^1H NMR (300 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.00 (dd, 7.2 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.90 (t, 8.0 Hz, 1H, $\text{C}\equiv\text{N}\text{C}$), 7.62 (dd, 7.2 and 1.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.53 (d, 8.0 Hz, 4H, $\text{C}\equiv\text{N}\text{C}$), 7.40 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.28 (dt, 7.3 and 1.3 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 2.49 (t, 6.9 Hz, 2H, $\text{CH}_2-(\text{CH}_2)_2-(\text{CH}_2)_2-\text{CH}_3$), 1.63-1.71 (m, 4H, $\text{CH}_2-(\text{CH}_2)_2-(\text{CH}_2)_2-\text{CH}_3$), 1.40 (m, 4H, $\text{CH}_2-(\text{CH}_2)_2-(\text{CH}_2)_2-\text{CH}_3$), 0.95 (t, 7.0 Hz, 3H, $\text{CH}_2-(\text{CH}_2)_2-(\text{CH}_2)_2-\text{CH}_3$); positive EI-MS: m/z 536 $[\text{M}]^+$; IR (KBr): 2155 cm^{-1} $\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{25}\text{H}_{24}\text{NAu}$ (found): C 56.08 (55.96), H 4.52 (4.60), N 2.62 (2.53).

$[\text{Au}(\text{C}\equiv\text{N}\text{C})\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{N}(\text{C}_6\text{H}_5)_2\text{-p}]$ (Compound 8)

[0064] Yield: 72%. Yield: 80%. ^1H NMR (300 MHz, CH_2Cl_2 , 298° K., relative to Me_4Si): δ 8.05 (dd, 7.2 and 1.2 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.92 (t, 8.0 Hz, 1H, $\text{C}\equiv\text{N}\text{C}$), 7.64 (dd, 7.2 and 1.2 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.56 (d, 8.0 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.48 (d, 8.8 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$), 7.42 (t, 7.2 Hz, 2H, $\text{C}\equiv\text{N}\text{C}$ H's), 7.32-7.26 (m, 6H, $\text{C}\equiv\text{N}\text{C}$, C_6H_4 and $\text{N}-\text{C}_6\text{H}_5$), 7.14-7.02 (m, 8H, $\text{C}\equiv\text{N}\text{C}$, C_6H_4 and $\text{N}-\text{C}_6\text{H}_5$); positive EI-MS: m/z 694 $[\text{M}]^+$; IR (KBr): 2143 cm^{-1} $\nu(\text{C}\equiv\text{C})$; elemental analyses calc'd for $\text{C}_{37}\text{H}_{25}\text{N}_2\text{Au}\cdot\frac{1}{2}\text{H}_2\text{O}$ (found): C 60.85 (61.10), H 3.67 (3.53), N 3.78 (3.80).

UV-Vis Absorption Properties

[0065] All the luminescent gold(III) compounds exhibit an intense absorption band at 312-327 nm and a moderately intense vibronic-structured absorption band at 362-426 nm in dichloromethane at 298° K. The photophysical data of 1-8 are summarized in Table 1. In general, the electronic absorption energies are insensitive to the nature of the alkynyl ligands. The low-energy vibronic-structured absorption band show vibrational progressional spacings of 1310-1380 cm^{-1} , corresponding to the skeletal vibrational frequency of the $\text{C}\equiv\text{N}\text{C}$ ligand. Such low-energy absorptions are assigned as intraligand (IL) $\pi-\pi^*$ transition. An additional shoulder appeared in each of the electronic absorption spectra of compounds 6 and 8 at ca. 415 and 426 nm, respectively (see **FIGS. 6 and 7**). Since the alkynyl ligand with electron-rich amino substituent has better electron-donating property, the presence of a low-lying alkynyl-to-diarylpyridine ligand-to-ligand charge transfer (LLCT) transition is possible. Thus the low-energy absorptions in compounds 6 and 8 are assigned as an admixture of intraligand (IL) $\pi-\pi^*(\text{C}\equiv\text{N}\text{C})/\text{LLCT } \pi(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{NR}_2\text{-p})\rightarrow\pi^*(\text{C}\equiv\text{N}\text{C})$ transition.

Photoluminescence Properties

[0066] Unlike most other Au(III) compounds which are non-emissive or only show luminescence at low temperature compounds, 1-8 display intense luminescence at 468-625 nm in the solution state at room temperature (Table 1). In general, the emission energies of the compounds were found to be insensitive to the nature of the alkynyl ligands (**FIGS. 1 and 2**). A vibronic-structured emission band with band maximum at 473 nm is observed for 1-5 and 7 in dichloromethane at room temperature. The vibrational progressional spacings of ca. 1300 cm^{-1} are in line with the $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$ stretching frequency of the tridentate ligand, indicative of the involvement of tridentate ligand in the excited state origin. Similar to the low-energy absorption band in the electronic absorption studies, the luminescence is assigned as originated from metal-perturbed intra-ligand $^3[\pi-\pi^*]$ state of the tridentate $\text{C}\equiv\text{N}\text{C}$ ligand. Compounds 6 and 8 exhibit a structureless emission band at lower energy in dichloromethane at room temperature (**FIGS. 3 and 4**). The emission spectra of compounds 1-8 in the solid state show a low-energy structureless band at around 570 nm (**FIGS. 4 and 5**). The red shift of the solid-state emission relative to that in the solution state is attributed to the excimeric intraligand emission arising from the π stacking of the $\text{C}\equiv\text{N}\text{C}$ ligand, probably due to the ordered packing of the molecules in the solid state.

TABLE 1

Photophysical data for Compounds 1 through 8.				
Compound	Medium (T[K])	Absorption λ_{max} [nm] ($\epsilon_{\text{max}}[\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}]$)	Emission λ_{max} [nm]	
1	CH_2Cl_2 (298)	312 (19890), 322 (19980), 364 (5050), 381 (5870), 402 (4870)	476, 506, 541, 582	
	Solid (298)		588	
	Thin film (298) ^a		568	

TABLE 1-continued

Photophysical data for Compounds 1 through 8.			
Compound	Medium (T[K])	Absorption λ_{max} [nm] (ϵ_{max} [dm ³ mol ⁻¹ cm ⁻¹])	Emission λ_{max} [nm]
2	CH ₂ Cl ₂ (298)	312 (19400), 322 (19640), 365(4640), 382(5170), 402(4305)	476, 506, 539, 584
3	Solid (298)		558
	CH ₂ Cl ₂ (298)	312 sh (27160), 327 (36005), 364 sh (17995), 382 sh (10170), 403 (5630)	477, 508, 546, 593
4	Solid (298)		563
	CH ₂ Cl ₂ (298)	312 (13820), 322 (13455), 362 (6400), 380 (6245), 400 (4190)	474, 505, 539, 584
5	Solid (298)		555
	CH ₂ Cl ₂ (298)	312 (17855), 322 (18100), 363 (5785), 381 (5945), 401 (4455)	475, 505, 538, 583
6	Solid (298)		556
	CH ₂ Cl ₂ (298)	310 (19195), 322 sh (15680), 365 (8855) 381 (10100), 399 (8300), 415 sh (3410)	611
7	Solid (298)		585
	CH ₂ Cl ₂ (298)	311 (14775), 320 (13925), 364 (3810), 380 (4900), 400 (4280)	473, 505, 537, 583
8	Solid (298)		555
	CH ₂ Cl ₂ (298)	312 (37090), 322 (38325), 364 (8525), 384 (10040), 400 (10035), 426 sh (4145)	625
	Thin film (298) ^a		564

^aprepared by vacuum deposition

EXAMPLE 2

[0067] FIG. 10A shows an illustrative OLED structure of device 1: ITO/4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) (60 nm)/compound 1 (30 nm)/aluminum tris(8-hydroxyquinoline) (Alq₃) (10 nm)/LiF (1 nm)/Al (90 nm). NPB and Alq₃ act as the hole transporting material and the electron transporting or injection material, respectively. Electroluminescence spectra of device 1 at different DC voltages applied are shown in FIG. 10B. In general, both the emission band of NPB in the range of 450-520 nm and the emission band of compound 1 at about 585 nm are observed upon application of DC voltage. At a lower DC voltage, the emission arising from compound 1 is more intense relative to the emission band of NPB. Upon increasing the DC voltage, the relative emission intensity ratio of compound 1: NPB decreases gradually. Therefore, the emission color of device 1 can be tuned from orange to green by applying different DC voltages.

EXAMPLE 3

[0068] FIG. 11A shows an illustrative OLED structure of device 2: ITO/N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1, 19-biphenyl]-4,4'-diamine (TPD) (70 nm)/compound 1 (10 nm)/Alq₃ (40 nm)/LiF (0.6 nm)/Al (150 nm). TPD acts as the hole transporting material. The electroluminescence spectrum of device 2 is depicted in FIG. 11B. The EL spectrum shows only one band at around 585 nm. The EL spectrum

compares well with the photoluminescence (PL) spectrum of compound 1 (FIG. 7), indicating that both EL and PL arise from the same excited state or the same type of exciton, which is attributed to the excimeric intraligand emission resulting from the π stacking of the C^{*}N^{*}C ligand. FIGS. 11C and 11D show the characteristics of device 2 with the relationship between current density, luminance and voltage; and between current, power efficiency and current density. The turn-on voltage is about 5 V.

EXAMPLE 4

[0069] FIG. 12A shows an illustrative OLED structure of device 3: ITO/TPD (70 nm)/compound 8 (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (30 nm)/Alq₃ (10 nm)/LiF (0.6 nm)/Al (150 nm). BCP acts as the hole blocking material. The electroluminescence spectrum of device 3 is depicted in FIG. 12B. The EL spectrum shows only one band at around 580 nm. The EL spectrum compares well with the photoluminescence (PL) spectrum of compound 8 (shown in FIG. 5), indicating that both EL and PL arise from the same excited state or the same type of exciton, which is attributed to the excimeric intraligand emission resulting from the π stacking of the C^{*}N^{*}C ligand. FIGS. 12C and 12D show the characteristics of device 3 with the relationship between current density, luminance and voltage; and between current, power efficiency and current density. The turn-on voltage is about 6.5 V. The relatively higher turn on voltage is due to the increase in emitting layer thickness (30 nm) and the introduction of an additional hole blocking layer.

EXAMPLE 5

[0070] FIG. 13A shows the general OLED structure: ITO/TPD (70 nm)/4,4'-N,N'-dicarbazole-biphenyl (CBP) doped with (X %) compound 8 (30 nm)/BCP (30 nm)/Alq₃ (10 nm)/LiF (0.6 nm)/Al (150 nm) [X=1 (device 4a), 3 (device 4b), 6 (device 4c), 12 (device 4d), 18 (device 4e), 100 (device 4f)]. CBP acts as the host material. FIG. 13B displays the normalized EL spectra of devices 4a-f with different concentration of compound 8 as dopant upon applying 12 V DC voltage. It is clear that the EL band shifts to red from 500 nm to 580 nm upon increasing the dopant concentration. Since the emitting layer in device 4 is fabricated by the simultaneous vacuum deposition of compound 8 and the host, a higher dopant concentration of compound 8 may give rise to a higher order and better packing of the molecules, leading to stronger π stacking of the C^{*}N^{*}C ligand, and hence a lower energy excimeric intraligand emission. Therefore, a dependence of the EL color on the dopant concentration of the luminescent gold(III) compound, leading to concentration-dependent color tuning, can be accomplished in the present invention.

EXAMPLE 6

[0071] Device 5 with the following OLED structure: ITO/TPD (70 nm)/CBP (compound 8, 6 wt %) (30 nm)/1,3,5-tris(2'-(1'-phenyl-1'-H-benzimidazole)benzene (TPBi) (60 nm)/LiF (1 nm)/Al (150 nm) is fabricated (FIG. 13). Higher efficiency is obtained in device 5 by using TPBi as electron transporting material which has higher mobility than Alq₃. The characteristics of device 5 are illustrated in FIG. 13B which shows (a) plot of current density and luminance versus voltage; (b) plot of current and power efficiency

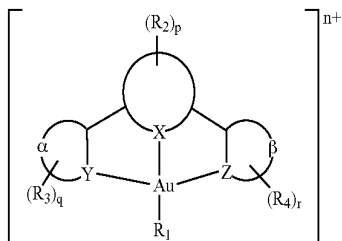
versus current density; and (c) plot of quantum efficiency versus current density. Inset: spectra characteristics of device 5.

1. A luminescent compound comprising a tridentate ligand and at least one strong σ -donating group coordinating to a gold(III) metal center.

2. A luminescent compound having the chemical structure represented by any of the following general formula (I), wherein R_1 - R_4 each independently represent the group containing hydrogen, halogen, alkynyl, substituted alkynyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, substituted alkoxy, amino, substituted amino, cyano, nitro, alkylcarbonyl, alkoxy carbonyl, arylcarbonyl, aryloxy carbonyl, mono- or dialkylaminocarbonyl, alkylcarbonyloxy, arylcarbonyloxy, aryloxy, alkoxy carbonyl, aryloxy carbonyloxy group, and the like; X, Y and Z each independently represent a heteroatom or a carbon;



represents an aromatic or heterocyclic 5- or 6-membered ring; α and β each independently represent a bridge for an aromatic or heterocyclic 5- or 6-membered ring or represent a break for non-cyclic moiety; C—X, C—Y and C—Z each independently represent a single bond or double bond; n represents a zero or an integer; p, q and r represent positive integers.



3. A compound according to claim 2 wherein said compound can be deposited as a thin film.

4. A compound according to claim 3 wherein said thin layer can be deposited by sublimation, vacuum deposition, or spin-coating.

5. A compound according to claim 2 wherein said compound has photoluminescence properties.

6. A compound according to claim 5 wherein said compound has electroluminescence properties.

7. A compound of claim 2 wherein said compound can be fabricated into a light-emitting device.

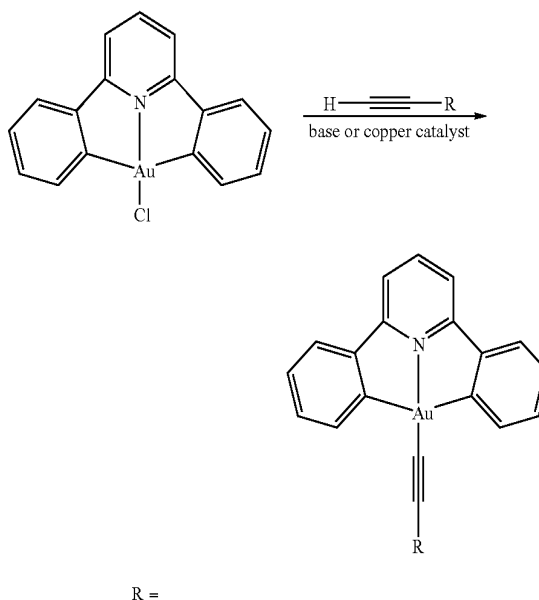
8. A light-emitting device wherein the compound of claim 2 is used as light-emitting layer.

9. A light-emitting device according to claim 8 wherein the compound of claim 2 is used as a dopant in the light-emitting layer.

10. A light-emitting device according to claim 8 wherein the luminescence color of the compound varies with the applied voltage.

11. A light-emitting device according to claim 9 wherein the luminescence band maximum of the compound varies with the concentration of the dopant.

12. A method for preparing a luminescent compound with a tridentate ligand and at least one strong σ -donating group coordinating to a gold(III) metal center, comprising the following reaction:



R =

C_6H_5	(1)
C_6H_4-Cl-p	(2)
$C_6H_4-NO_2-p$	(3)
$C_6H_4-OCH_3-p$	(4)
$C_6H_4-C_6H_{13}-p$	(5)
$C_6H_4-NH_2-p$	(6)
C_6H_{13}	(7)
$C_6H_4-N(C_6H_5)_2-p$	(8)

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